SHAPE-SELECTIVE HYDROGENATION OF NAPHTHALENE
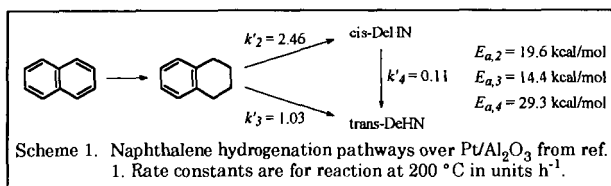## OVER ZEOLITE-SUPPORTED Pt AND Pd CATALYSTS

Andrew D. Schmitz, Grainne Bowers and Chunshan Song

Department of Materials Science and Engineering
Fuel Science Program, 209 Academic Projects Building
Pennsylvania State University, University Park, PA 16802

Introduction

Per-hydrogenation of naphthalene produces both cis-decalin (c-DeHN) and trans-decalin (t-DeHN). Huang and Kang reported the rate data shown in Scheme 1 for this reaction catalyzed by Pt/Al$_2$O$_3$.[1] Isomerization of c-DeHN was treated as irreversible, and it was assumed that dehydrogenation of DeHN could be neglected. We have found it possible to achieve high selectivity

Scheme 1. Naphthalene hydrogenation pathways over Pt/Al$_2$O$_3$ from ref. 1. Rate constants are for reaction at 200 °C in units h^{-1}.

for one DeHN isomer by appropriate catalyst selection. For example, Pt/HY gives 100% naphthalene conversion to decalins with 80% selectivity for c-DeHN. There numerous potential industrial applications for c-DeHN; such as, the production of sebacic acid which can be used in the manufacture of Nylon 6,10 and softeners. Conversely, catalysts that promote the thermodynamically favored c-DeHN to t-DeHN isomerization can be made to give nearly 95% t-DeHN. This reaction can be used in fuel upgrading applications, to increase the thermal stability of the fuel.

Considerable effort has been invested in this laboratory to develop jet fuels with improved thermal stability, particularly for high-performance jet aircraft (see ref. 2, for example). In this application, the fuel is also used as the primary heat sink for cooling. As the fuel temperature is raised, fuel degradation leads to the formation of solid particulates in the fuel.[2] Over time, the particulates agglomerate and are deposited, plugging filters, fuel lines and fuel injectors. A jet fuel's overall carbon-forming propensity can be reduced by limiting its aromatic content as in the complete hydrogenation of naphthalene. In thermal stressing of jet fuels, Song et al. have shown that cyclic alkanes have higher thermal stability than normal alkanes.[2-3] Cycloalkane conformation also effects high temperature stability, and it has been shown that t-DeHN is more stable than c-DeHN.[2-3] Tests on the thermal stressing of petroleum-derived fuels and model compounds have shown that addition of t-DeHN can significantly retard the rate of carbon deposition.[3]

Two types of zeolites were used in this work: H-mordenite (HM) and HY. Mordenite has a two-dimensional channel structure with elliptically shaped channels of diameter 6.7 x 7.0 Å. Since naphthalene's critical diameter is very close to the HM channel dimension, transition state selectivity is induced on reactions of naphthalene occurring in the channels. Relative diffusion rates of the products can also effect selectivity. HY has large cavities in its interior and narrow channel openings. A reactant that has entered the channel structure may reorient itself and react at catalyst sites on the walls of the cavities. However, because of restricted diffusion at the channel openings, only molecules of appropriate diameter will be produced at an appreciable rate.

The final t-DeHN/c-DeHN (t/c) ratio in the product is governed by several factors related to the bifunctionality of the catalysts. While the initial t/c ratio may be governed by several factors, zeolite acid character significantly influences c-DeHN isomerization. It has been found that catalysts based on dealuminated HM give the highest t-DeHN selectivity. Choice of the noble metal, Pt or Pd, is also important. In accord with previously reported data for naphthalene hydrogenation using noble metal catalysts on non-zeolite supports,[4] our data show that Pd/zeolite has higher initial selectivity for t-DeHN, and also isomerize c-DeHN at higher rates than platinum on the same zeolite. Metal particle sizes determined from X-ray powder diffraction (XRD) line-widths show large variations on the different zeolites.

Experimental

Catalyst Preparation. The zeolites were supplied in NH$_4$-form and used as received. Table 1 lists their properties. Two portions of each zeolite were loaded with metal, one with Pt, the other Pd, to generate a total of eight catalysts. Incipient wetness impregnation of either aqueous H$_2$PtCl$_6$.xH$_2$O (Aldrich, 99.995% Pt, metal basis) or PdCl$_2$ (Aldrich, 99.999% Pd, metal basis) dissolved in dilute hydrochloric acid (sufficient to form soluble PdCl$_4$$^{2-}$) was used to achieve a nominal metal concentration of 6 wt%. Following drying in vacuo, the catalysts were calcined in

air at 450 °C for 2 h. Noble metal reduction occurs during the catalyst test, in the hydrogen pressurized reactors.

Catalyst Evaluation. A 30 mL, stainless steel tubing-bomb batch reactor was used for catalyst tests. A tee-shaped design was used where most of the reactor internal volume is in the horizontal member that contains the catalyst and reactants. The horizontal member is connected by a 10" length of 1/4" o.d. tubing to a pressure gauge and valve. The reactor was charged with 0.4 g catalyst, 1.0 g (7.8 mmol) naphthalene (Aldrich, 99%), 4.0 g n-tridecane reaction solvent, and 0.35 g n-nonane internal standard. The charged reactor was flushed with H_2 then sealed and leak-tested with H_2. Finally, the hydrogen pressure was adjusted to 1500 psig cold (ca. 0.2 g) to start the test. Naphthalene begins to react immediately, even at room temperature, so a consistent procedure was established to minimize the time between reactor pressurization and the start of the run.

The reactor was affixed to a holder and placed in a fluidized sand-bath heater so that approximately two-thirds of the total length was immersed. Vertical agitation at 240 cycle/min was used to provide mixing. The reactions were done at 200 °C for 6-60 min. At the end of each test, the reaction was quenched in cold water. After cooling, the gas headspace was collected for analysis and the reactor was opened. Acetone was used to wash the reactor contents onto a filter and the filtrate was analyzed by GC/GC-MS (30m x 0.25mm DB-17 column, J&W Scientific), while the solid was dried for XRD examination.

X-ray powder diffraction analyses (XRD) were done on a Scintag 3100 diffractometer using Cu Kα radiation and a scan rate of 1° 2θ /min with 0.02° steps. Diffraction line widths were measured using a profile-fitting program which assumes a peak shape intermediate between Gaussian and Cauchy. Manual measurements were always used to check the calculated results, especially for very diffuse lines where the computer routine fails. Mean metal crystallite size was calculated by application of the Scherrer equation (wavelength 1.54056 Å, Scherrer constant 0.89).[5] Silicon powder (-325 mesh) was used as an external standard for measuring instrumental and spectral broadening. Kα$_2$-doublet broadening corrections, and pure line profile determination for low-angle reflections were done as described elsewhere.[6] For most of the catalysts, only the Pt or Pd (111) diffraction line was suitable for profile analysis. The lower intensity lines of the metals were interfered with by zeolite patterns.

Results and Discussion

XRD Observations. XRD for the Pt and Pd catalysts removed from the reactors following the 60 min runs are shown in Figures 1-2. In each case, only diffraction lines corresponding to the zero-valency state of the metals are observed. Several catalysts from the 30 min runs were also examined, and only metallic phase is observed. Therefore, in situ hydrogen treatment is adequate for complete metal reduction. Differences between the samples are striking, especially for the Pt catalysts. Pt/HY shows very sharp and intense metal diffraction lines (large Pt particles), but Pt/HM38 and Pt/HM17 show very broad, diffuse lines indicative of small Pt particles. Pt/M21 is intermediate. Closer examination of Pt/HM38 shows that the Pt-phase is bidisperse. A sharp line appears superimposed over a very broad band, both arising from reduced platinum. Pd catalysts (Figure 1) all show significant line-broadening. The trend in line width increase on going from metal/HY to metal/HM17 is also observed for Pd, but is less pronounced. Average metal particle sizes for the Pt and Pd catalysts are compared in Table 2 and Table 3, respectively.

Accuracy of the XRD particle size technique is generally accepted to be ± 10-20%. When XRD lines become very broad and diffuse, accurate line-width measurements are difficult, however. This was more of a problem for Pd which has a lower scattering power ($z = 46$) than Pt ($z = 78$). Baseline zeolite signals from HM38 and HM17 cloud the Pd (111) reflection enough that accurate measurements are not possible. Conservatively narrow best-guesses at the line widths were used to determine the values cited in the tables.

Effects of Catalyst Composition. Test data for 60 min runs at 200 °C for the eight Pt- and Pd-loaded zeolite catalysts are compared in Table 2 and Table 3, respectively. The products of Nap hydrogenation are almost exclusively isomeric DeHN's. In some cases, a small amount of tetrahydronaphthalene (TeHN) is observed. Gas headspace analyses show 5-50 ppm levels of C_1-C_4 hydrocarbons. Every catalyst gives ca. 100% Nap conversion in 1 h, so it is not possible to rank catalyst activity based on these data. Yet, the trans/cis DeHN ratio is highly dependent on both the zeolite and the metal. Palladium gives higher t-DeHN selectivity than platinum on the same zeolite. Catalysts based on HM38 gave the highest t-DeHN selectivity. There is a definite upward trend in t/c ratio with HM SiO$_2$/Al$_2$O$_3$ ratio. Pt/HY shows amazingly high selectivity for c-DeHN.

Comparing catalyst with the same metal, there does not seem to be any correlation between metal crystallite size and DeHN isomer selectivity. Neither naphthalene hydrogenation nor c-DeHN isomerization involve C-C σ-bond breaking. Consequently, the overall reaction should be structure insensitive and independent of metal particle size.

Effects of Run Duration. In order to determine the practical equilibrium t/c ratio, four tests were done with Pd/HM21 at extended reaction times (Table 4). An approximately constant t/c of 13.6 is obtained within 6 h reaction time. This value is somewhat lower than the calculated equilibrium constant for c-DeHN to t-DeHN isomerization of 20.5 at 200 °C.[6] However, ca. 14 is the practical limit as confirmed using other Pt/zeolite and Pd/zeolite catalysts.[7] Some decalin may reside in the portion of the reactor that extends above the sand level in the fluidized sand bath, *the cold zone,* and may not react. According to calculations, if even 5% of the decalin doesn't react to form an equilibrium amount of t-DeHN, the equilibrium constant value falls to 13.0.[6]

It was already known that complete naphthalene conversion to a mixture of decalins occurred within the first hour of each test. We wanted to find out if the initial product distribution was significantly different than what we had observed in 60 min runs. Additional runs were done with Pt/HM38, Pd/HM38, PtHY and Pd/HY at 15 and 30 min. The metal/HY catalysts were also tested at 6 min. It should be noted that 6 min is the approximate time required for the interior of the reactor to equilibrate to the reaction (sand bath) temperature. Greater than 99% naphthalene conversion occurred within the shortest run period for each test. Decalins were the only hydrogenation products with the exception of the 6 min run with Pt/HY, where 48% TeHN was also observed. However, less than 3 % TeHN was observed in the longer runs with Pt/HY. Plots of log(c-DeHN) vs time are linear (Figure 3) showing that the isomerization of c-DeHN is first-order. Considering Scheme 1, when all of the TeHN has been consumed, the rate expression for disappearance of c-DeHN simplifies to a simple first-order expression in c-DeHN concentration. This simplification does not hold when the TeHN concentration is non-zero, so the 6 min data point for Pt/HY is not included in the determination of k_4. Values determined for the rate constant in this work are compared with literature values in Table 5. It can be seen that not only does Pd have a higher initial selectivity for t-DeHN, but it also isomerizes t-DeHN faster than Pt. The values of k_4 determined in this work are considerably higher than those reported by Huang and Kang,[1] and Lai and Song for direct isomerization of c-DeHN.[6] Huang and Kang did not report the mass of catalyst used, so it is not possible to compare values on a per-gram catalyst basis. Lai and Song used the same Pt/HM38 catalyst that was used here. We are still not certain what causes the discrepancy between these data and the results of Lai and Song. Other detailed kinetic studies on hydrogenation of aromatics have recently been published.[8-9]

The Pt/HY catalyst is highly selective for c-DeHN and does not promote the isomerization. We are unable to explain this result at present but suspect that it may be due, in some way, to the large Pt particle size (1700 Å). It is possible that a unique type of shape-selectivity may arise from partial blockage of the channel openings by the large metal particles. Further understanding may be gained by electron microscopy and H_2 chemisorption to determine metal dispersions.

Conclusions

It has been established that the naphthalene hydrogenation process can be tailored to produce either c-DeHN or t-DeHN by appropriate choice of the zeolite and metal species. Selectivity for t-DeHN increases with SiO_2/Al_2O_3 ratio in the HM catalysts, so that catalysts based on HM38 gave the highest t-DeHN selectivity. Compared to Pt on a given zeolite, Pd shows a higher initial selectivity for t-DeHN, and a higher rate for c-DeHN to t-DeHN isomerization. The practical equilibrium t/c ratio is 14 at 200 °C. Metal crystallite sizes are highly dependent on the zeolite. Pd generally had a higher dispersion than did platinum on a given zeolite. Naphthalene hydrogenation and c-DeHN isomerization are structure insensitive reactions. Therefore, DeHN isomer selectivity does not show a correlation with particle size. Uniquely high selectivity for c-DeHN has been obtain with Pt/HY. It has been proposed that partial channel blockage by the large metal particles of this catalysts give rise to a unique type of shape-selectivity.

Acknowledgements

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Table 1. Properties of the Zeolite Starting Materials

zeolite id.	zeolite type	supplier	SiO_2/Al_2O_3, molar	Na_2O, wt %	surface area, m^2/g
HY	zeolite Y	Linde LZ-Y62	5.0	2.5	948
HM17	mordenite	Linde LZ-M-8	17.0	0.05	480
HM21	mordenite	PQ Corp., Inc. CBV 20A	21.1	0.02	606
HM38	mordenite	PQ Corp., Inc. CBV 30A	37.5	0.07	512

Table 2. Naphthalene Hydrogenation Data for Platinum Catalysts in 60 min Runs at 200 °C

catalyst	conv., %	Product Distribution (mole %)				trans/cis DeHN	average metal particle size, Å
		TeHN	trans-DeHN	cis-DeHN	total DeHN		
Pt/HM17	100	0.0	37	63	100	0.58	120
Pt/HM21	100	0.0	45	55	100	0.83	590
Pt/HM38	100	0.0	70	30	100	2.34	50 (750)[a]
Pt/HY	100	2.6	15	82	97	0.18	1700

[a] Bidisperse metal. Particle sizes for the broad (and sharp) components of the Pt (111) are indicated.

Table 3. Naphthalene Hydrogenation Data for Palladium Catalysts in 60 min Runs at 200 °C

catalyst	conv., %	Product Distribution (mole %)				trans/cis DeHN	average metal particle size, Å
		TeHN	trans-DeHN	cis-DeHN	total DeHN		
Pd/HM17	100	0.0	65	35	100	1.84	< 60[a]
Pd/HM21	100	0.0	75	25	100	3.00	310
Pd/HM38	100	0.0	82	18	100	4.42	< 60[a]
Pd/HY	100	0.0	73	27	100	2.69	310

[a] Diffuse diffraction line makes accurate width measurement difficult. Metal particles are no larger than the indicated size.

Table 4. Equilibrium DeHN Isomer Distribution from Naphthalene Hydrogenation Over Pd/HM21 Catalyst at 200 °C

time (h)	conv., %	Product Distribution (mole %)				trans/cis DeHN
		TeHN	trans-DeHN	cis-DeHN	total DeHN	
1	100	0.0	76.5	23.5	100	3.26
6	100	0.0	93.1	6.92	100	13.46
10	100	0.0	93.2	6.78	100	13.74
24	100	0.0	93.2	6.85	100	13.59

Table 5. Comparison of c-DeHN Isomerization
Rate Constants from This Work and the Literature

	Pt/HM38	Pd/HM38	Pt/HY	Pd/HY	Pt/HM38[a]	Pt/Al$_2$O$_3$[b]
k_4, h^{-1}	0.78	0.84	0	0.35	0.30	0.11
k_4, mmol/g·cat·h	15.2	16.4	0	6.9 ·	10.9	—

[a]Isomerization of c-DeHN from ref. 6. [b]Naphthalene hydrogenation from ref. 1.
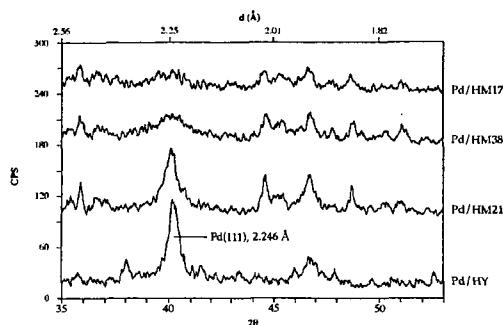
Figure 1.   XRD patterns for palladium catalysts in the region of
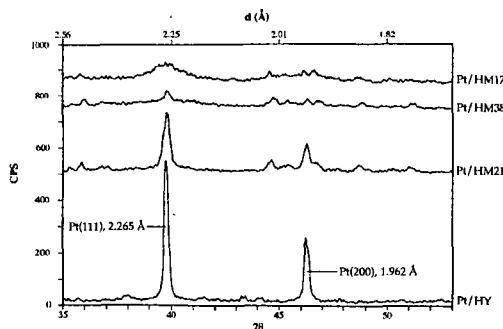the Pd (111) and (200) lines.

Figure 2.   XRD patterns for platinum catalysts in the region of
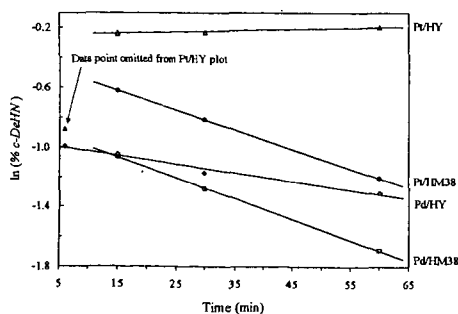the Pt (111) and (200) lines.

Figure 3. First-order rate constant plots for c-DeHN to t-
DeHN isomerization at 200 °C.